

APPLICATION FOR UNITED STATES LETTERS PATENT

for

IMPROVED METHOD FOR REDUCING THE CARBON MONOXIDE
CONTENT OF A HYDROGEN RICH GAS

by

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BACKGROUND OF THE INVENTION

Fuel cells provide electricity from chemical oxidation-reduction reactions and possess significant advantages over other forms of power generation in terms of cleanliness and efficiency. Typically, fuel cells employ hydrogen as the fuel and oxygen as the oxidizing agent. The power generation is proportional to the consumption rate of the reactants.

A significant disadvantage which inhibits the wider use of fuel cells is the lack of a widespread hydrogen infrastructure. Hydrogen has a relatively low volumetric energy density and is more difficult to store and transport than the hydrocarbon fuels currently used in most power generation systems. One way to overcome this difficulty is the use of reformers to convert the hydrocarbons to a hydrogen rich gas stream which can be used as a feed for fuel cells.

Hydrocarbon-based fuels, such as natural gas, LPG, gasoline, and diesel, require conversion processes to be used as fuel sources for most fuel cells. Current art uses multi-step processes combining an initial conversion process with several clean-up processes. The initial process is most often steam reforming (SR), autothermal reforming (ATR), catalytic partial oxidation (CPOX), or non-catalytic partial oxidation (POX).

As a practical matter, the hydrogen rich gas also contains other chemical species such as nitrogen, hydrogen sulfide, carbon monoxide, carbon dioxide, and carbonyl sulfide. For many uses, such as fuel for fuel cells or as feed to an ammonia plant, carbon monoxide levels must be reduced greatly. Catalyst enhanced water-gas shift reaction steps are generally used to reduce the carbon monoxide level to 0.1 to 0.5 mole%. For uses that require lower concentrations of carbon monoxide, a common practice is to oxidize the carbon monoxide to carbon dioxide by the addition of air to the hydrogen rich product gas in the presence of catalysts that promote the oxidation of carbon monoxide over the oxidation of hydrogen to water. As commonly practiced this method of removing carbon monoxide can result in large losses of hydrogen if the heat produced by the exothermic oxidation process is not removed since the catalysts used tend to become less specific for carbon monoxide oxidation as the temperature increases. In addition, if the temperature is too low, the carbon monoxide can deactivate the catalyst.

Despite the above work, there remains a need for a simple unit for use with a fuel cell – one that can produce hydrogen rich gas with minimal carbon monoxide impurity.

SUMMARY OF THE INVENTION

The present invention utilizes a porous distribution tube to add air for carbon monoxide oxidation throughout the length of a catalyst bed. By distributing the air injection, hot and cold areas in the catalyst bed can be avoided, thereby improving the selectivity of the reactor to carbon monoxide oxidation.

One illustrative embodiment of the present invention includes a method and apparatus for reducing the carbon monoxide content of a hydrogen rich gas having a catalyst bed containing an oxidation catalyst, a porous tube positioned substantially within the catalyst bed for distributing an oxygen-containing stream throughout the catalyst bed, and a cooling jacket for maintaining the reactor operating temperature in a desired range. The porous tube can be constructed as a sintered stainless steel tube or as an alumina tube or as any equivalent porous tube that is known to those of skill in the art to perform the objectives of this method and apparatus. The porous tube is positioned along the catalyst bed length, or may be aligned in any orientation that one of skill in the art would appreciate to result in optimal dispersion of the oxygen-containing stream throughout the catalyst bed. In one illustrative embodiment of the present invention is for the reactor operating temperature to be controlled by the cooling jacket from about 90°C to about 180°C, more preferably from about 90°C to about 150°C. The cooling jacket should contain a circulating coolant that can be water, steam, or air, or, in one illustrative embodiment, the hydrocarbon fuel feed to the fuel processor for energy efficiency.

BRIEF DESCRIPTION OF THE DRAWINGS

The description is presented with reference to the accompanying drawings in which:

FIG. 1 depicts a simple process flow diagram for a fuel processor.

FIG. 2 illustrates an improved apparatus and method for selectively oxidizing carbon monoxide in accordance with the present invention

1 **DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS**

2

3 The present invention is generally directed to an improved method for reducing the
4 carbon monoxide content of a hydrogen rich gas stream. In one illustrative embodiment,
5 the present invention uses a porous distribution tube to add an oxygen-containing stream
6 for the carbon monoxide oxidation throughout the length of a catalyst bed instead of one
7 or two fixed injection points as is currently practiced. By distributing the air injection hot
8 and cold areas in the catalyst bed can be avoided, thereby improving the selectivity of the
9 reactor to carbon monoxide oxidation. In one illustrative embodiment of the present
10 invention, the apparatus and methods described relate to improved reduction of the
11 carbon monoxide content of a hydrogen rich gas stream in a compact fuel processor for
12 feeding a fuel cell. Hydrogen rich gas produced from such compact fuel processors will
13 have increasing importance in the development of fuel cells, including fuel cells used to
14 power automotive vehicles. Accordingly, while the invention is described herein as being
15 used in conjunction with compact fuel processors and fuel cells, the scope of the
16 invention is not limited to such use.

17 The hydrocarbon fuel feed to a fuel processor may be liquid or gas at ambient
18 conditions as long as it can be vaporized. As used herein the term "hydrocarbon"
19 includes organic compounds having C-H bonds that are capable of producing hydrogen
20 from a partial oxidation or steam reforming reaction. The presence of atoms other than
21 carbon and hydrogen in the molecular structure of the compound is not excluded. Thus,
22 suitable fuels for use in the method and apparatus disclosed herein include, but are not
23 limited to hydrocarbon fuels such as natural gas, methane, ethane, propane, butane,
24 naphtha, gasoline, and diesel fuel, and alcohols such as methanol, ethanol, propanol, and
25 the like.

26 The fuel processor feeds include hydrocarbon fuel, oxygen, and water. The
27 oxygen can be in the form of air, enriched air, or substantially pure oxygen. The water
28 can be introduced as a liquid or vapor. The composition percentages of the feed
29 components are determined by the desired operating conditions, as discussed below.

30 The fuel processor effluent stream includes hydrogen and carbon dioxide and can
31 also include some water, unconverted hydrocarbons, carbon monoxide, impurities (e.g.

hydrogen sulfide and ammonia) and inert components (e.g., nitrogen and argon, especially if air was a component of the feed stream).

Figure 1 depicts a general process flow diagram for a fuel processor. One of skill in the art should appreciate that a certain amount of progressive order is needed in the flow of the reactants through the reactors disclosed herein.

Process step A is an autothermal reforming process in which two reactions, partial oxidation (formula I, below) and optionally also steam reforming (formula II, below), are combined to convert the feed stream F into a synthesis gas containing hydrogen and carbon monoxide. Formulas I and II are exemplary reaction formulas wherein methane is considered as the hydrocarbon:



The partial oxidation reaction occurs very quickly to the complete conversion of oxygen added and produces heat. The steam reforming reaction occurs slower and consumes heat. A higher concentration of oxygen in the feed stream favors partial oxidation whereas a higher concentration of water vapor favors steam reforming. Therefore, the ratios of oxygen to hydrocarbon and water to hydrocarbon become characterizing parameters. These ratios affect the operating temperature and hydrogen yield.

The operating temperature of the autothermal reforming step can range from about 550°C to about 900°C, depending on the feed conditions and the catalyst. The invention uses a catalyst bed of a partial oxidation catalyst with or without a steam reforming catalyst. The catalyst may be in any form including pellets, spheres, extrudate, monoliths, and the like. Partial oxidation catalysts should be well known to those with skill in the art and are often comprised of noble metals such as platinum, palladium, rhodium, and/or ruthenium on an alumina washcoat on a monolith, extrudate, pellet or other support. Non-noble metals such as nickel or cobalt have been used. Other washcoats such as titania, zirconia, silica, and magnesia have been cited in the literature. Many additional materials such as lanthanum, cerium, and potassium have been cited in the literature as “promoters” that improve the performance of the partial oxidation catalyst.

1 Steam reforming catalysts should be known to those with skill in the art and can
2 include nickel with amounts of cobalt or a noble metal such as platinum, palladium,
3 rhodium, ruthenium, and/or iridium. The catalyst can be supported, for example, on
4 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination.
5 Alternatively, the steam reforming catalyst can include nickel, preferably supported on
6 magnesia, alumina, silica, zirconia, or magnesium aluminate, singly or in combination,
7 promoted by an alkali metal such as potassium.

8 Process step B is a cooling step for cooling the synthesis gas stream from process
9 step A to a temperature of from about 200°C to about 600°C, preferably from about
10 300°C to about 500°C, and more preferably from about 375°C to about 425°C, to
11 optimize the temperature of the synthesis gas effluent for the next step. This cooling may
12 be achieved with heat sinks, heat pipes or heat exchangers depending upon the design
13 specifications and the need to recover / recycle the heat content of the gas stream. One
14 illustrative embodiment for step B is the use of a heat exchanger utilizing feed stream F
15 as the coolant circulated through the heat exchanger. The heat exchanger can be of any
16 suitable construction known to those with skill in the art including shell and tube, plate,
17 spiral, etc. Alternatively, or in addition thereto, cooling step B may be accomplished by
18 injecting additional feed components such as fuel, air or water. Water is preferred
19 because of its ability to absorb a large amount of heat as it is vaporized to steam. The
20 amounts of added components depend upon the degree of cooling desired and are readily
21 determined by those with skill in the art.

22 Process step C is a purifying step. One of the main impurities of the hydrocarbon
23 stream is sulfur, which is converted by the autothermal reforming step A to hydrogen
24 sulfide. The processing core used in process step C preferably includes zinc oxide and/or
25 other material capable of absorbing and converting hydrogen sulfide, and may include a
26 support (e.g., monolith, extrudate, pellet etc.). Desulfurization is accomplished by
27 converting the hydrogen sulfide to water in accordance with the following reaction
28 formula III:



30 Other impurities such as chlorides can also be removed. The reaction is
31 preferably carried out at a temperature of from about 300°C to about 500°C, and more

1 preferably from about 375°C to about 425°C. Zinc oxide is an effective hydrogen sulfide
2 absorbent over a wide range of temperatures from about 25°C to about 700°C and affords
3 great flexibility for optimizing the sequence of processing steps by appropriate selection
4 of operating temperature.

5 The effluent stream may then be sent to a mixing step D in which water is
6 optionally added to the gas stream. The addition of water lowers the temperature of the
7 reactant stream as it vaporizes and supplies more water for the water gas shift reaction of
8 process step E (discussed below). The water vapor and other effluent stream components
9 are mixed by being passed through a processing core of inert materials such as ceramic
10 beads or other similar materials that effectively mix and/or assist in the vaporization of
11 the water. Alternatively, any additional water can be introduced with feed, and the
12 mixing step can be repositioned to provide better mixing of the oxidant gas in the CO
13 oxidation step G disclosed below.

14 Process step E is a water gas shift reaction that converts carbon monoxide to
15 carbon dioxide in accordance with formula IV:



17 This is an important step because carbon monoxide, in addition to being highly
18 toxic to humans, is a poison to fuel cells. The concentration of carbon monoxide should
19 preferably be lowered to a level that can be tolerated by fuel cells, typically below 50
20 ppm. Generally, the water gas shift reaction can take place at temperatures of from
21 150°C to 600°C depending on the catalyst used. Under such conditions, most of the
22 carbon monoxide in the gas stream is converted in this step.

23 Low temperature shift catalysts operate at a range of from about 150°C to about
24 300°C and include for example, copper oxide, or copper supported on other transition
25 metal oxides such as zirconia, zinc supported on transition metal oxides or refractory
26 supports such as silica, alumina, zirconia, etc., or a noble metal such as platinum,
27 rhenium, palladium, rhodium or gold on a suitable support such as silica, alumina,
28 zirconia, and the like.

29 High temperature shift catalysts are preferably operated at temperatures ranging
30 from about 300° to about 600°C and can include transition metal oxides such as ferric
31 oxide or chromic oxide, and optionally including a promoter such as copper or iron

1 silicide. Also included, as high temperature shift catalysts are supported noble metals
2 such as supported platinum, palladium and/or other platinum group members.

3 The processing core utilized to carry out this step can include a packed bed of
4 high temperature or low temperature shift catalyst such as described above, or a
5 combination of both high temperature and low temperature shift catalysts. The process
6 should be operated at any temperature suitable for the water gas shift reaction, preferably
7 at a temperature of from 150°C to about 400°C depending on the type of catalyst used.
8 Optionally, a cooling element such as a cooling coil may be disposed in the processing
9 core of the shift reactor to lower the reaction temperature within the packed bed of
10 catalyst. Lower temperatures favor the conversion of carbon monoxide to carbon
11 dioxide. Also, a purification processing step C can be performed between high and low
12 shift conversions by providing separate steps for high temperature and low temperature
13 shift with a desulfurization module between the high and low temperature shift steps.

14 Process step F is a cooling step performed In one illustrative embodiment by a
15 heat exchanger. The heat exchanger can be of any suitable construction including shell
16 and tube, plate, spiral, etc. Alternatively a heat pipe or other form of heat sink may be
17 utilized. The goal of the heat exchanger is to reduce the temperature of the gas stream to
18 produce an effluent having a temperature preferably in the range of from about 90°C to
19 about 150°C.

20 Oxygen is added to the process in step F. The oxygen is consumed by the
21 reactions of process step G described below. The oxygen can be in the form of air,
22 enriched air, or substantially pure oxygen. The heat exchanger may by design provide
23 mixing of the air with the hydrogen rich gas. Alternatively, the embodiment of process
24 step D may be used to perform the mixing.

25 Process step G is an oxidation step wherein almost all of the remaining carbon
26 monoxide in the effluent stream is converted to carbon dioxide. The processing is carried
27 out in the presence of a catalyst for the oxidation of carbon monoxide and may be in any
28 suitable form, such as pellets, spheres, monolith, etc. Oxidation catalysts for carbon
29 monoxide are known and typically include noble metals (e.g., platinum, palladium)
30 and/or transition metals (e.g., iron, chromium, manganese), and/or compounds of noble
31 or transition metals, particularly oxides. A preferred oxidation catalyst is platinum on an

alumina washcoat. The washcoat may be applied to a monolith, extrudate, pellet or other support. Additional materials such as cerium or lanthanum may be added to improve performance. Many other formulations have been cited in the literature with some practitioners claiming superior performance from rhodium or alumina catalysts. Ruthenium, palladium, gold, and other materials have been cited in the literature as being active for this use.

Two reactions occur in process step G: the desired oxidation of carbon monoxide (formula V) and the undesired oxidation of hydrogen (formula VI) as follows:



The preferential oxidation of carbon monoxide is favored by low temperatures. Since both reactions produce heat it may be advantageous to optionally include a cooling element such as a cooling coil disposed within the process. The operating temperature of process is preferably kept in the range of from about 90°C to about 150°C. Process step G preferably reduces the carbon monoxide level to less than 50 ppm, which is a suitable level for use in fuel cells, but one of skill in the art should appreciate that the present invention can be adapted to produce a hydrogen rich product with higher and lower levels of carbon monoxide.

The effluent exiting the fuel processor is a hydrogen rich gas containing carbon dioxide and other constituents which may be present such as water, inert components (e.g., nitrogen, argon), residual hydrocarbon, etc. Product gas may be used as the feed for a fuel cell or for other applications where a hydrogen rich feed stream is desired. Optionally, product gas may be sent on to further processing, for example, to remove the carbon dioxide, water or other components.

In one illustrative embodiment of the above described fuel processor, a compact fuel processor is of modular construction with individual modular units, which are separable, rearrangeable, and individually replaceable.

The present invention is an improvement to process step G described above, and utilizes a porous distribution tube to add air for the carbon monoxide oxidation throughout the catalyst bed length instead of one or two fixed injection points. By distributing the air injection hot and cold areas in the catalyst bed can be avoided.

1 Referring to the oxidation reactor 200 in Figure 2, air A is injected through a
2 porous tube 210, such as a sintered stainless steel tube manufactured by the Mott
3 Corporation or an alumina tube as manufactured by the NGK corporation of Japan. By
4 maintaining the air supply at a slightly higher pressure than the hydrogen rich gas feed H,
5 supply air A will enter the chamber containing a carbon monoxide selective oxidation
6 catalyst 220, such as that manufactured by the Engelhard Corporation. Upon coming into
7 contact with the catalyst 220, the oxygen in the air will oxidize carbon monoxide and
8 hydrogen (according to equations V and VI, above) causing the catalyst 220 and reactor
9 200 to warm. By using a cooling jacket 230 containing water, steam, air, or a cool
10 hydrocarbon fuel feed stream, reactor 200 can be maintained in the desired operating
11 temperature range of from about 90°C to about 180°C. This oxidation step preferably
12 reduces the carbon monoxide level to less than 50 ppm, which is a suitable level for use
13 in fuel cells, but one of skill in the art should appreciate that the present invention can be
14 adapted to produce a hydrogen rich product P with higher and lower levels of carbon
15 monoxide.

16 In view of the above disclosure, one of skill in the art should understand and
17 appreciate that one illustrative embodiment of the present invention includes a method
18 and apparatus for reducing the carbon monoxide content of a hydrogen rich gas. Such an
19 illustrative embodiment includes a catalyst bed containing an oxidation catalyst, a porous
20 tube positioned substantially within the catalyst bed for distributing an oxygen-containing
21 stream throughout the catalyst bed, and a cooling jacket for maintaining the reactor
22 operating temperature in a desired range. The porous tube can be constructed as a
23 sintered stainless steel tube or as an alumina tube or as any equivalent porous tube that is
24 known to those of skill in the art to perform the objectives of this method and apparatus.
25 The porous tube is positioned along the catalyst bed length, or may be aligned in any
26 orientation that one of skill in the art would appreciate to result in optimal dispersion of
27 the oxygen-containing stream throughout the catalyst bed. In one illustrative
28 embodiment of the present invention is for the reactor operating temperature to be
29 controlled by the cooling jacket from about 90°C to about 180°C, more preferably from
30 about 90°C to about 150°C. The cooling jacket should contain a circulating coolant that

1 can be water, air, or the hydrocarbon fuel to the fuel processor for energy efficiency
2 improvements.

3 The present invention is intended not only for general oxidation reactors, but is
4 also a preferred technology selection for the carbon monoxide oxidation reactors of fuel
5 processors. Because of the direct feed to a fuel cell, there is a great need to ensure
6 continuous on-specification hydrogen rich gas produced from compact fuel processors.

7 While the apparatus, compositions and methods of this invention have been
8 described in terms of preferred or illustrative embodiments, it will be apparent to those of
9 skill in the art that variations may be applied to the process described herein without
10 departing from the concept and scope of the invention. All such similar substitutes and
11 modifications apparent to those skilled in the art are deemed to be within the scope and
12 concept of the invention as it is set out in the following claims.